



The characterization of organic nitrogen and sulfur functional groups in coals after biomethane production

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Abstract

To study the change characteristics of nitrogen and sulfur functional types in the raw coal and coal residues after anaerobic fermentation, three different rank coals from Baiyinhua mine (BY coal), Qianqiu mine (QQ coal), and Malan mine (ML coal) in China were collected and treated with methanogenic microorganisms, then X-ray photoelectron spectroscopy (XPS) was used to test the nitrogen and sulfur functional types in raw coals and coal residues. The results show that the pyrrolic nitrogen (N-5) and aromatic sulfur are the main nitrogen type and sulfur type in three coals. The N-5 increases by 17.42% in BY coal residue and decreases by 2.37% and 8.51% in QQ and ML coal residues, respectively. The pyridinic nitrogen (N-6) in BY, QQ, and ML coal residues decreases by 2.18%, 5.44%, and 2.75%, respectively. The aromatic sulfur increases by 2.13%, 3.14%, and 4.02% in BY, QQ, and ML coal residues, respectively. The aliphatic sulfur has obvious changes in BY and QQ coal residues with the increment of 9.17% and decrement of 11.64%, respectively. The results reveal that the nitrogen and sulfur types have changed in the coal residues after the biomethane production, and the instable types such as N-5 and aliphatic sulfur have obvious changes in the low-rank BY and QQ coals. The research provides a sight to the changes about nitrogen and sulfur types after biomethane yield and more deep thoughts about the clean and effective utilization of coals.

Keywords Coal · Biomethane · X-ray photoelectron spectroscopy · Nitrogen types · Sulfur types

Introduction

Coal is an important fossil fuel, but the combustion of coal will cause air pollution due to the release of NO_x , N_2O , SO_2 , etc. (Sui et al. 2018). The organic nitrogen and sulfur in coal exist as a variety of chemical forms, and many researchers have shown that the occurrence state of organic nitrogen is mainly pyridinic nitrogen, pyrrolic nitrogen, quaternary nitrogen, and oxidized organic nitrogen, while the organic sulfur is mainly aliphatic sulfur, aromatic sulfur, sulfoxide, and sulfones (Kawashima et al. 2013; Li et al. 2015;

Wang et al. 2016; Phiri et al. 2018). The chemical forms of nitrogen and sulfur would influence the reactivity of coals because of their different structures and stability (Kambara et al. 1993; Zhang et al. 2014). High-rank coals usually show a high content of quaternary nitrogen and aromatic sulfur (Burchill and Welch 1989; Kelemen et al. 2006; 2008). After pyrolysis, the nitrogen functions tend to present in char as pyridinic nitrogen and quaternary nitrogen, and the aromatic sulfur needs a higher decomposition temperature than aliphatic sulfur (Valentim et al. 2011). The precursor researches of SO_2 and NO_x in the combustion of coal have shown that the aliphatic sulfur is much easier to convert into H_2S than aromatic sulfur, and the HCN is mainly attributed to the conversion of relatively unstable structure of pyridinic nitrogen, while the NH_3 is mainly originated from the relatively stable organic nitrogen, such as pyrrolic nitrogen (Nelson 1992; Kelemen et al. 1993; Leppälähti and Koljonen 1995; Wójtowicz et al. 1995; Sun et al. 1997, 2002; Chang et al. 2004; Xie et al. 2005).

Biogenic methane is found in the coal-bearing basins all over the world and is a very important composition of coalbed methane (Strapoć et al. 2011; Guo et al. 2019).

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In an anaerobic environment, the coal macromolecules are degraded by methanogenic microorganisms into small molecules (such as formic acid, acetic acid, H_2 , and CO_2) which can be directly utilized as a substrate by methanogenic archaea (Flores et al. 2008; Penner et al. 2010; Davis et al. 2019). Then the biogenic methane would be synthesized by three optional metabolic pathways associated to the types of methanogenic archaea: (1) acetate metabolism pathway, (2) methyl nutrition pathway, and (3) carbon dioxide reduction pathway (Fang et al. 2015). The bioconversion research of coal is very meaningful to produce more clean fuel of methane, and it has derived some new energy technologies, such as the microbially enhanced coal-bed methane technology (Ritter et al. 2015). However, so far, the nitrogen and sulfur functional types in the coal residues after biomethane yield have hardly been studied.

In the present study, the X-ray photoelectron spectroscopy (XPS) technology was used to study the characteristics of nitrogen and sulfur functional types in coals before and after

anaerobic fermentation, and then the environmental effect of nitrogen and sulfur types was discussed.

Materials and methods

Coal samples

The coal lumps were collected from Baiyinhua mine of Inner Mongolia, Qianqiu mine of Henan, Malan mine of Shanxi, in China, respectively (Fig. 1). The coals were loaded into sterile and sealed glass containers and then transported to the laboratory for reserving and using. The proximate and ultimate analyses were performed according to the ISO 17246–2010 and ISO 17247–2013 standards. Vitrinite reflectance measurement was carried out using incident light polarized at 45° and the reflected light passing through a 546-nm band filter on the path to the photomultiplier. The photometer was calibrated against a series of glass standards of known reflectance (Table 1).

Fig. 1 The locations of different coal samples

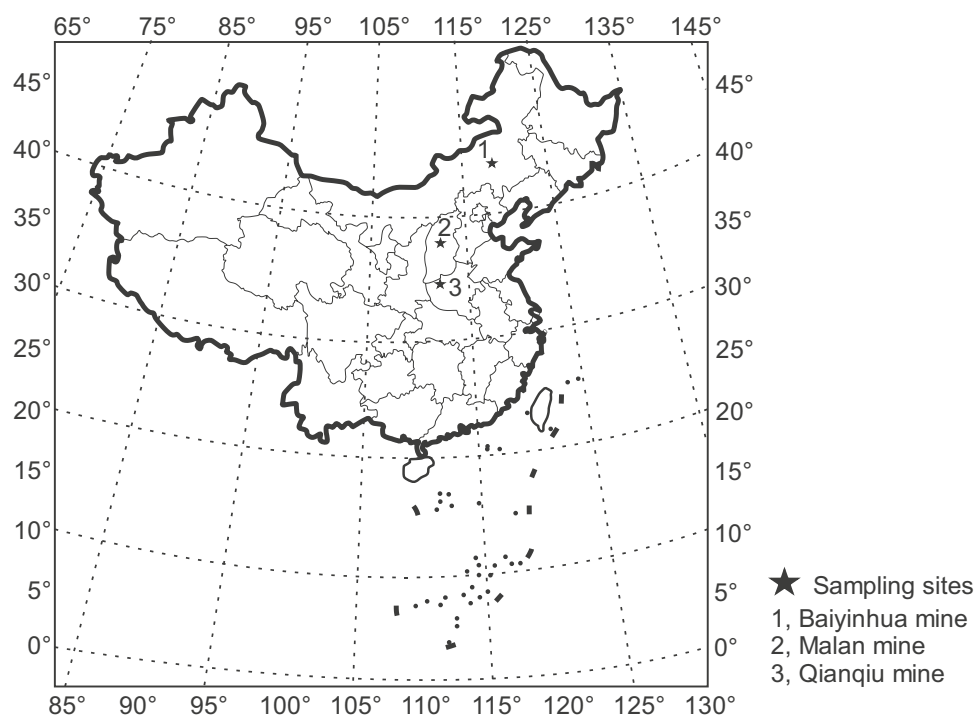


Table 1 The proximate and ultimate analyses of coal samples (%)

Sampling mine	Coal labels	M_{ad}	A_{ad}	V_{daf}	$R_{o,max}$	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}
Baiyinhua mine	BY	3.41	14.63	41.53	0.43	67.14	5.52	24.63	1.83	0.88
Qianqiu mine	QQ	0.98	10.31	40.01	0.56	71.89	4.71	20.74	1.02	1.66
Malan mine	ML	0.74	19.88	20.82	1.10	90.39	4.69	2.82	0.48	1.63

M , moisture; A , ash; V , volatile; $R_{o,max}$, vitrinite maximum reflectance; ad, air dry basis; daf, dry-ash free basis

Microbial treatment

The methanogens were cultured from the fresh coalbed water with methanogenic bacteria enrichment medium. Methanogenic bacteria enrichment medium: 1.0 g NH_4Cl , 0.1 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.4 g $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, 0.2 g KH_2PO_4 , 0.2 g Na_2S , 2.0 g NaHCO_3 , 0.001 g $\text{C}_{12}\text{H}_7\text{NO}_4$, 0.5 g $\text{C}_3\text{H}_7\text{NO}_2\text{S}$, 2.0 g HCOONa , 2.0 g CH_3COONa , 1.0 g yeast extract, 0.1 g tryptone, and 10 mL trace element solution were added to 1000 mL coal seam water. Trace element solution: 1000 mL sterile deionized water contained 1.5 g triglycolamic acid, 0.5 g $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, 3.0 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1.0 g NaCl , 0.1 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.1 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01 g H_3BO_3 , 0.01 g $\text{KAl}(\text{SO}_4)_2$, 0.02 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.01 g Na_2MoO_4 .

Then the mixture of pulverized coal (0.18–0.25 mm) and the enrichment solution of methanogens at a ratio of 1 g coal:10 mL solution was stirred well in a glass conical flask of 250 mL, and the conical flask was sealed in the atmosphere of nitrogen as a fermentation device. Then the device was put into an incubator for fermentation at a constant temperature of 35°C, and the anaerobic fermentation process continued for about 36 days. Coal residues of 36 days of fermentation were washed using distilled water and dried in the vacuum drying oven at 80°C for 24 h.

X-Ray photoelectron spectroscopy

The nitrogen and sulfur functional types in raw coal and coal residues after anaerobic fermentation for 36 days were tested by XPS technology. The XPS analysis was performed using Thermo Scientific Escalab 250 Xi (Thermo Fisher Scientific Technology (China) Co., Ltd., Beijing, China) equipped with $\text{AlK}\alpha$ radiation source ($h\nu = 1486.6$ eV). The transmission energy of survey scan and narrow scan is 100 eV and 30 eV, respectively. The binding energy of nitrogen and sulfur was calibrated according to the binding energy of $\text{C}1s$ (285 eV). The nitrogen and sulfur spectra curves were deconvoluted using the software XPSpeak 4.1.

Biogas detection

The biogas production in the anaerobic fermentation of coal was measured by drainage gas gathering method. The

Table 2 The biogas production of different coal samples

Coal samples	Biogas production (mL)	Methane concentration (%)	Methane production (mL/g coal)
BY coal	212.50	34.01	3.61
QQ coal	144.20	27.09	1.95
ML coal	130.50	10.47	0.68

methane concentration was tested using a gas chromatograph (Agilent 7890 GC; Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a Carbonplot chromatographic column and a TCD detector.

Results and discussion

Biogas production

The biogenic methane production after anaerobic fermentation was shown in Table 2 and Fig. 2. The results show that the coals from Baiyinhua mine, Qianqiu mine, and Malan mine have different biogas production. The BY coal exhibits the highest biogas production of 212.5 mL and methane concentration of 34.01% in three coals. The biogas production and methane concentration of QQ coal are 144.20 mL and 27.09%, respectively. Also, the ML coal takes up the lowest biogas production of 130.50 mL and methane concentration of 10.47%. The results indicate that the biomethane production of coal in the anaerobic fermentation has an upward trend with the increase of coal rank.

Organic nitrogen

The N1s envelope was deconvoluted with mixed Gaussian–Lorentzian functions (30% Lorentzian and 70% Gaussian) for four sub-peaks named N-6 sub-peak, N-5 sub-peak, N-Q1 sub-peak, and N-X sub-peak, and their binding energy was constrained at 398.8 ± 0.3 eV, 400.6 ± 0.3 eV, 401.3 ± 0.3 eV, and 403.6 ± 0.3 eV respectively. The full width at half maximum of the sub-peak was fixed at 1.4 eV (Boudou et al. 2008; Wang et al. 2016) (Fig. 3). The relative

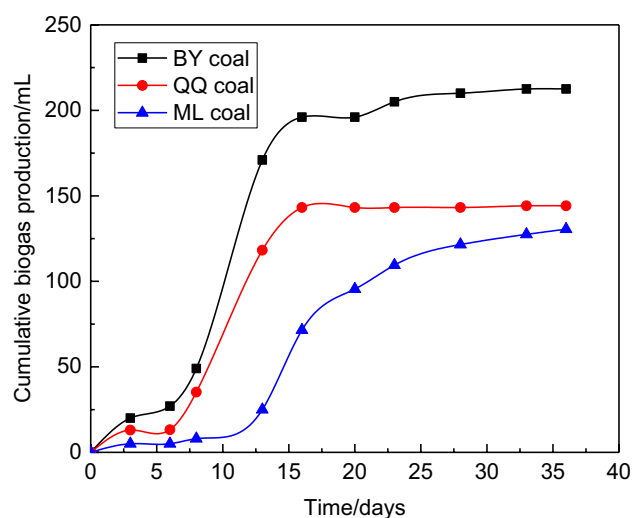


Fig. 2 The cumulative biogas production of different coals

content of the organic nitrogen is shown in Table 3 and Fig. 4.

The N-6 sub-peak attributes to pyridinic nitrogen where a nitrogen atom substitutes for a carbon atom in an aromatic ring (Pels et al. 1995; Casanovas et al. 1996) (Fig. 5). Figure 4 shows that compared to raw coals after anaerobic fermentation for 36 days, the pyridinic nitrogen in BY, QQ, and ML coal residues decreases by 2.18%, 5.44%, and 2.75%, respectively.

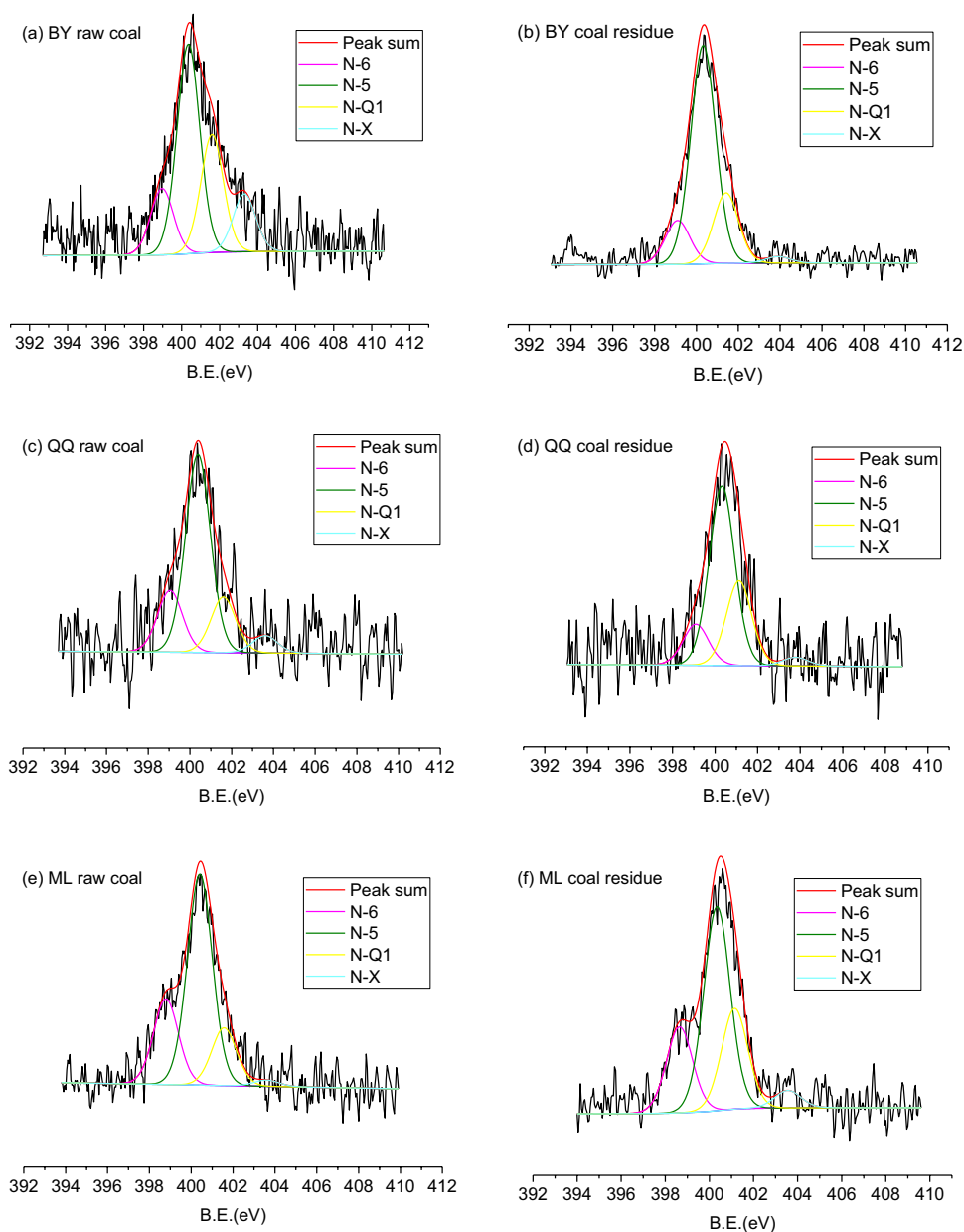
The N-5 sub-peak is related to three kinds of organic nitrogen: (1) pyrrolic nitrogen where a nitrogen atom substitutes a carbon atom in a no-aromatic ring or partially aromatic ring system with or without oxygen-containing substituents and the nitrogen atom is just bonded to one

Table 3 XPS results for the N1s curve resolution

Samples	Relative peak area (%)			
	N-6	N-5	N-Q1	N-X
BY raw coal	15.16	46.93	24.46	13.45
BY coal residue	12.98	64.35	20.72	1.95
QQ raw coal	18.53	59.51	16.73	5.22
QQ coal residue	13.09	57.14	27.02	2.76
ML raw coal	23.78	58.43	16.06	1.73
ML coal residue	21.03	49.92	24.76	4.28

hydrogen atom and two carbon atoms; (2) pyridinic nitrogen with oxygen-containing substituents such as hydrated

Fig. 3 The fitting curves of nitrogen spectra



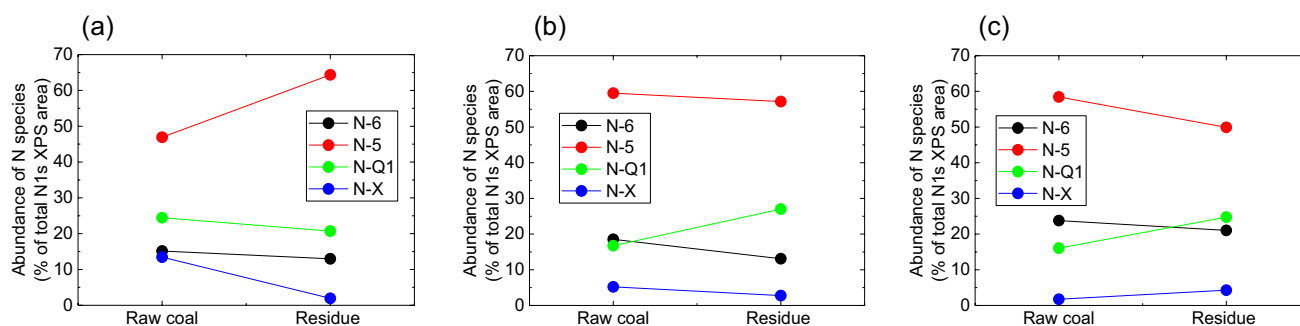


Fig. 4 The abundance of the nitrogen types before and after anaerobic fermentation in BY coal (a), QQ coal (b), and ML coal (c)

pyridinic rings, pyridone, and pyridine carboxylic acids; (3) amine and amide. Henceforth, it is referred to pyrrolic nitrogen peak because XPS technology cannot distinguish pyrrolic, amide, amines, and pyridone structures (Boudou et al., 2008; Valentim et al. 2011). Figure 4 shows that pyrrolic nitrogen occupies the highest organic nitrogen content in three coals, which is consistent with previous studies (Li et al. 2015). Compared to raw coals, the pyrrolic nitrogen in residue of BY coal after 36 days of anaerobic fermentation obviously increases by 17.42%. The pyrrolic nitrogen in residue of QQ and ML coals has a similar trend of decrease, in which the pyrrolic nitrogen content in QQ and ML residues decreases by 2.37% and 8.51%, respectively.

The N-Q1 sub-peak is associated with quaternary nitrogen (named N-C₃) where the nitrogen atom substitutes the carbon atom in condensed aromatic ring system and each nitrogen is bonded to three carbon atoms. The quaternary nitrogen has a higher binding energy than pyrrolic and

pyridinic nitrogen due to its three coordinated nitrogen structures (Boudou et al., 2008). Figure 4a shows that the quaternary nitrogen in residues of BY coal decreases by 3.74% compared to BY raw coal. Figure 4b and c shows that QQ and ML coal residues have a higher quaternary nitrogen amount than raw coals with increment of 10.29% and 8.7%, respectively.

The N-X sub-peak is usually assigned to the pyridinic N-oxide complexes with a high binding energy between 402 and 405 eV, but a form of quaternary nitrogen at a higher binding energy and fixed ammonium in clay may also be the candidate. Here, the binding energy of N-X was constrained at 403.6 ± 0.3 eV according to previous studies (Boudou et al. 2008; Valentim et al. 2011). Figure 4 shows that the amount of N-X in three coals is less than other organic nitrogen types. BY raw coal obviously has a higher amount of N-X than QQ raw coal and ML raw coal. The N-X in residue of BY coal after 36 days of anaerobic fermentation obviously decreases by 11.5%, and the N-X in QQ coal continuously declines from 5.22% in raw coal to 2.76% in coal residue. The N-X in residue of ML coal exhibits a trend of increase with increment of 2.55%.

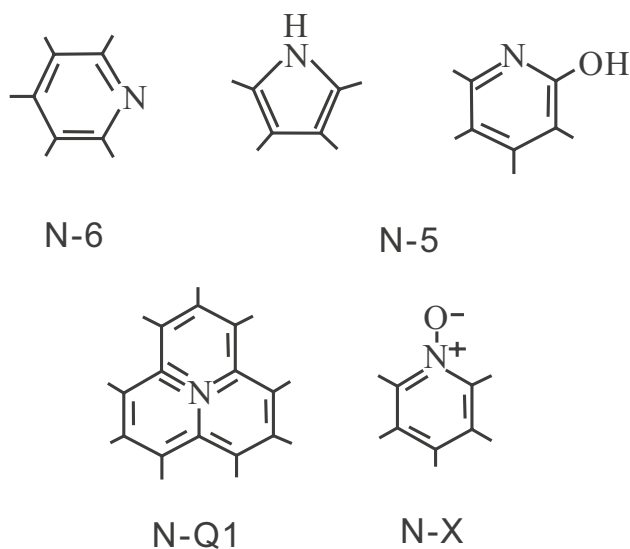


Fig. 5 Schematic nitrogen-containing molecular structures

Organic sulfur

The S2p envelope was deconvoluted with mixed Gaussian–Lorentzian functions (0% Lorentzian and 100% Gaussian) for four sub-peaks corresponding to aliphatic sulfur, aromatic sulfur, sulfoxide, and sulfones with binding energy of 162.8–163.5 eV, 164.0–164.2 eV, 165–166.5 eV, and 167.5–168.5 eV, respectively. The full width at half maximum of the sub-peak was fixed at 1.2 eV (Castro-Marcano and Mathews 2011; Li et al. 2015, 2017; Wang et al. 2016) (Fig. 6). The relative content of the organic sulfur is shown in Table 4 and Fig. 7.

The typical structure of aliphatic sulfur includes thiol and thioether. Thiol is a kind of non-aromatic compound with the structure of R-S-H (R respective carbon atom) and thioether has a general structure of R-S-R' (R and R' respective carbon

atom) (Fig. 8). Figure 7 shows that the aliphatic sulfur in residue of BY coal after 36 days of anaerobic fermentation increases by 9.17%; the aliphatic sulfur in residue of QQ coal decreases by 11.64% and increases by 4.64% in residue of ML coal.

The aromatic sulfur has a more stable structure such as thiophenic sulfur which is a five-membered heterocyclic compound containing one sulfur heteroatom. Figure 7 shows that the aromatic sulfur in three coals contributes to the major organic sulfur. The aromatic sulfur in BY, QQ, and ML coal residues increases by 2.13%, 3.14%, and 4.02%, respectively, after 36 days of anaerobic fermentation.

The sulfoxide expresses a general structure of $R-(S=O)-R'$ which can be produced by the oxidation of thioether and the sulfur atom is bonded to two carbon atoms. In contrast to raw coal, the sulfoxide in BY coal residue decreases by 7.13%; the sulfoxide in QQ coal residue increases by 6.16%; the sulfoxide in ML coal residue decreases by 5.95%.

The formation of sulfones ($R-S(=O)_2-R'$) is originated from the sulfonyl group with two carbon atoms which has a higher oxidation state than sulfoxide. For example, the dimethyl sulfide oxidizes first to get dimethyl sulfoxide and continues to oxidize to get dimethyl sulfone (the simplest compounds in sulfones). Figure 7a shows that the sulfones

Fig. 6 The fitting curves of sulfur spectra

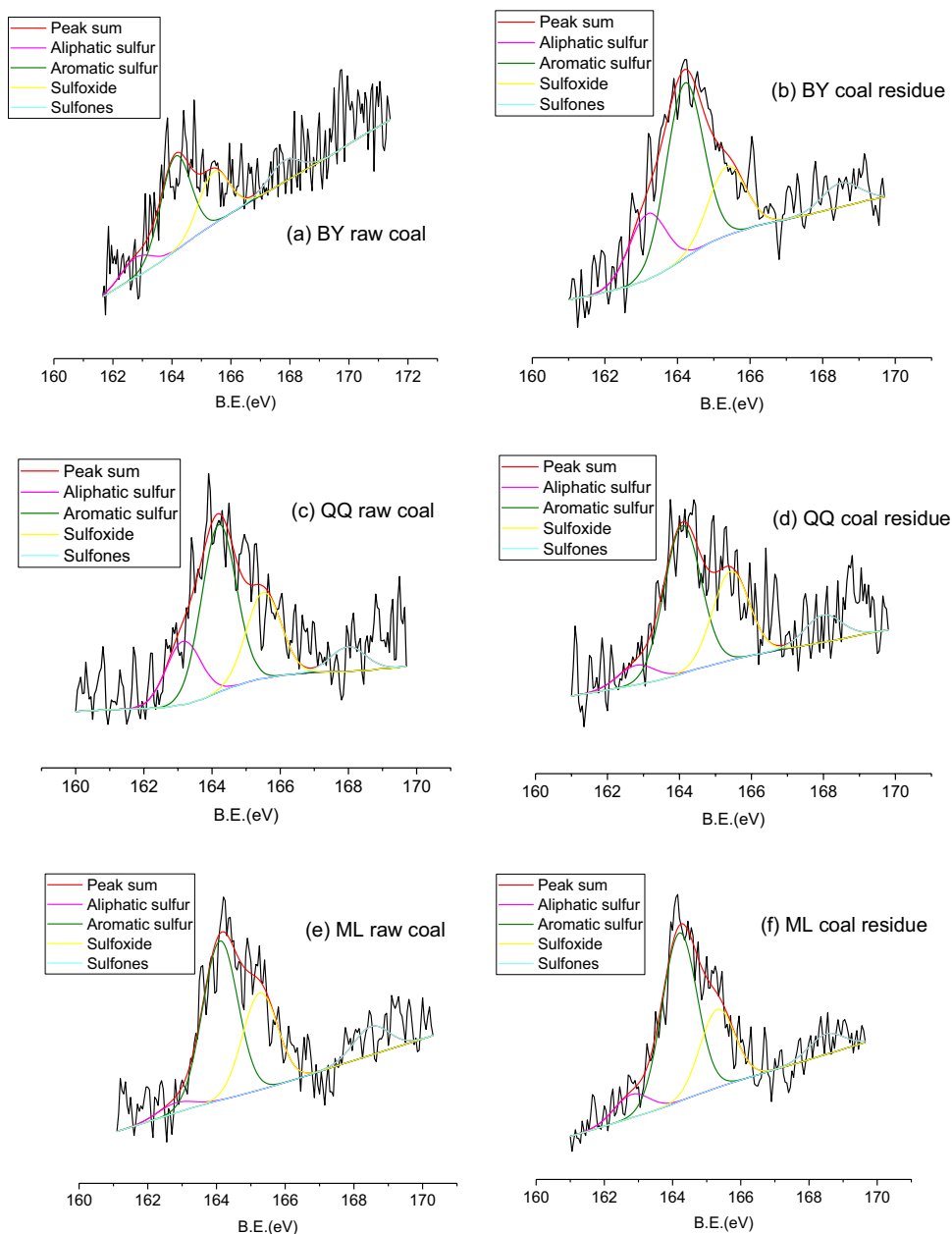


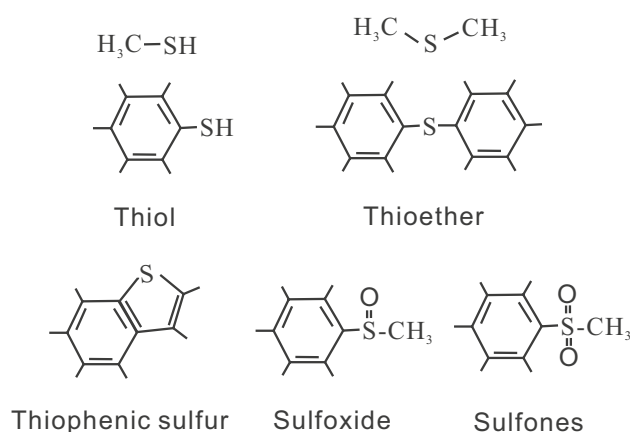
Table 4 XPS results for the S2p curve resolution

Samples	Relative peak area (%)			
	Aliphatic sulfur	Aromatic sulfur	Sulfoxides	Sulfones
BY raw coal	10.50	50.31	27.80	11.39
BY coal residue	19.67	52.44	20.67	7.22
QQ raw coal	18.53	49.04	25.19	7.24
QQ coal residue	6.89	52.18	31.35	9.57
ML raw coal	3.40	53.99	32.90	9.71
ML coal residue	8.04	58.01	26.95	7.01

in residue of BY coal decrease by 4.17%. Figure 7b shows that the sulfones in QQ coal residue increases by 2.33%. Figure 7c shows that the sulfones in ML coal residue decreases by 2.7% compared to raw coal.

Influence of coal metamorphic degree on nitrogen and sulfur types distribution

Some studies have shown that the metamorphic degree could influence the nitrogen and sulfur types in coals due to their different stability. In the high metamorphic degree, organic nitrogen tends to exist in the interior of the aromatic carbon layer as a more stable structure of N-C₃(N-Q1) (Boutique et al. 1984; Kelemen et al. 1994, 2006). However, the experiment of Boudou et al. (2008) also showed that N-Q1 began to increase exponentially just when C_{daf} was about more than 90% or R_{max} was about more than 2%, while the N-6 and N-5 increased and N-Q1 decreased when C_{daf} was about less than 90% or R_{max} was less than 2% (Boudou et al., 2008). The R_{max} of BY, QQ, and ML raw coals does not exceed the inflection point (R_{max} = 2%). It accords with the expectations that with the increase of R_{max}, the N-6 in BY, QQ, and ML raw coals shows an increase trend and N-Q1 shows a decrease trend, and the N-5 in BY raw coal is less than that in QQ and ML raw coals (Fig. 9). Some researchers

**Fig. 8** Schematic sulfur-containing molecular structures

have shown that aromatic sulfur is more stable than aliphatic sulfur, and low rank coals have less aromatic sulfur and more aliphatic sulfur than high rank coals (Kelemen et al. 1991; Li et al. 2015). Figure 9 shows that the aromatic sulfur in ML raw coal at high rank is more than that in BY and QQ coals at relative low rank stage, while BY and QQ raw coals have a higher content of aliphatic sulfur than ML raw coal, but the aliphatic sulfur in QQ raw coal is obviously more than BY raw coal.

The metamorphic degree is a significant factor that influences the biodegradation of coal by methanogens. Studies have shown that the low rank coals are more convenient to be degraded by methanogens than high rank coals due to the higher biological availability (Fallgren et al. 2013; Robbins et al. 2016). It is demonstrated by the biomethane production of 3.61 mL/g, 1.95 mL/g, and 0.68 mL/g of BY, QQ, and ML coals, respectively, in the 36-day anaerobic fermentation. The different biodegradation degree should have a performance on the change of nitrogen and sulfur types in the three coals. The absolute change values of relative content of N-5 in BY, QQ, and ML coal residues are 17.42%, 2.37%, and 8.51%, respectively (Fig. 10a). For the lowest-rank BY coal, the instable N-5 takes up the biggest

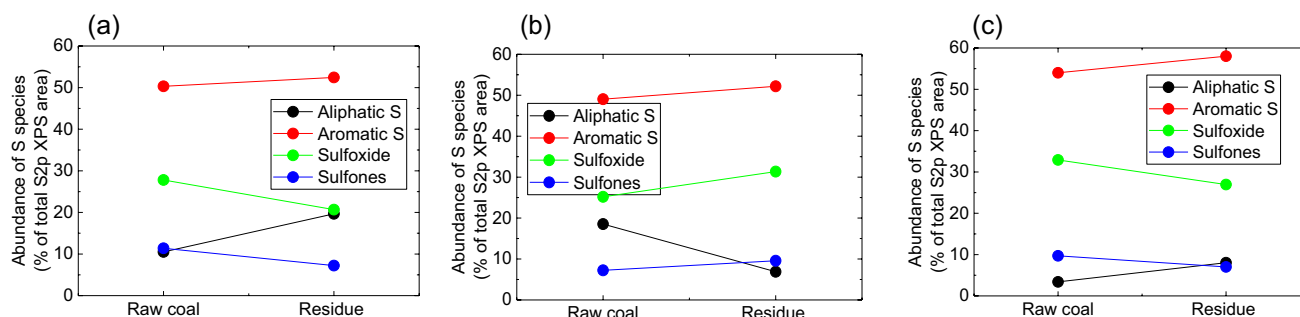
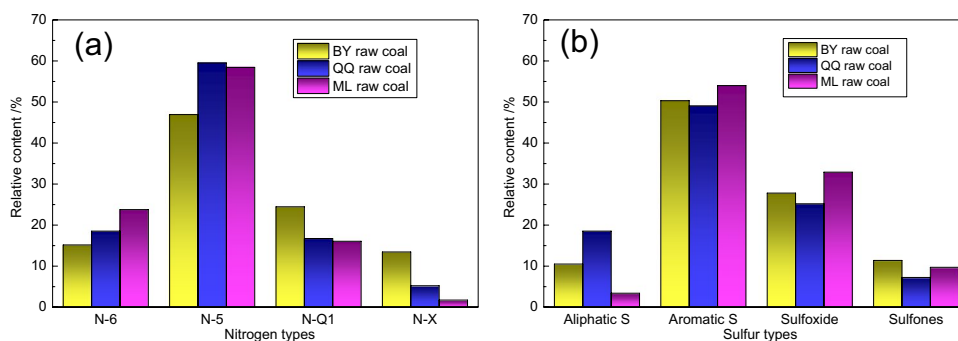
**Fig. 7** The abundance of the sulfur types before and after anaerobic fermentation in BY coal (a), QQ coal (b), and ML coal (c)

Fig. 9 The content of nitrogen types (a) and sulfur types (b) in raw coals



change value compared to the other nitrogen types, while the N-Q1 has the maximum variation in QQ coal residue and ML coal residue with the absolute change values of 10.29% and 8.7%, respectively. The BY residue and QQ residue show the high absolute change values of aliphatic sulfur with 9.17% and 11.64%, while the sulfoxide in the ML coal residue has a high absolute change value of 5.95% (Fig. 10b). The results reveal that the N-5 and aliphatic sulfur in relatively low metamorphic coal (such as BY and QQ coal) have a larger absolute change value, which is related to the high biodegradation of lower rank coals and the low stability of N-5 and aliphatic sulfur.

Environment effect of nitrogen and sulfur types in coal after methane generation

According to the mechanism of biomethane production (Liu and Whitman 2008), the terminal products are not only CH_4 , H_2O , CO_2 , but also H_2S and NH_3 (Table 5). The metabolic reaction could be seemed as an element removal process of carbon, hydrogen, oxygen, nitrogen, sulfur, etc., attributing to the microbial participation. So, the nitrogen and sulfur also should not be neglected in the metabolic process, and the types of nitrogen and sulfur in coals may be influenced by the electron transfer and the breaking or forming of the

chemical bonds involved. Moreover, some denitrifying bacteria and sulfate-reducing bacteria could appear in the complex microbial community of producing biomethane that would also make an influence on the nitrogen and sulfur in coal.

The types of nitrogen and sulfur are involved in the heat utilization of coal. In the pyrolysis process, N-6 is more stable than N-5, and N-5 ring would open firstly to HCN. NH_3 tends to mainly be formed by the transfer of N-6, and also may be formed by the transfer of N-Q1 and HCN. HCN and NH_3 are important precursors for fuel- NO_x formation (Nelson 1992; Leppälähti and Koljonen 1995; Wójtowicz et al. 1995; Chang et al. 2004; Xie et al. 2005). According to the release temperature of pyrolysis and activation energy, aliphatic sulfur compounds are easier to convert into H_2S than aromatic sulfides, and thiophene sulfur is the most difficult to remove (Kelemen et al. 1993; Sun et al. 1997, 2002). So, it is thought that the increase of N-6, instable N-5 and aliphatic sulfur may have a potential to enhance the formation of fuel- NO_x and SO_2 . On the other hand, the change of atomic content of nitrogen and sulfur in coal residues should also control the formation of fuel- NO_x and SO_2 , despite the change of types of nitrogen and sulfur in coal residues after anaerobic fermentation; if the atomic content of nitrogen and sulfur in coal residues decreases, the fuel- NO_x and SO_2 may

Fig. 10 The absolute change value of relative content of nitrogen types (a) and sulfur types (b) before and after anaerobic fermentation

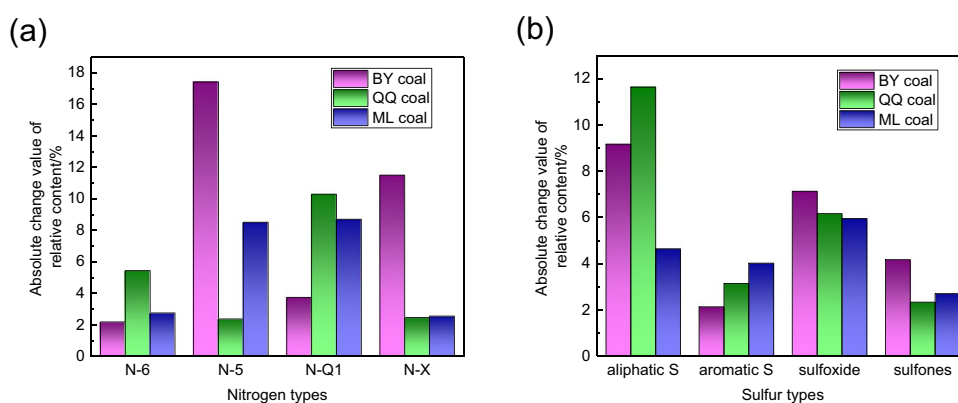


Table 5 The typical methanogenesis reactions and organisms (Liu and Whitman 2008)

Reaction pathways	Organisms
CO ₂ -type	
4H ₂ + CO ₂ → CH ₄ + 2H ₂ O	Most methanogens
4HCOOH → CH ₄ + 3CO ₂ + 2H ₂ O	Many hydrogenotrophic methanogens
CO ₂ + 4isopropanol → CH ₄ + 4acetone + 2H ₂ O	Some hydrogenotrophic methanogens
4CO + 2H ₂ O → CH ₄ + 3CO ₂	<i>Methanothermobacter</i> and <i>Methanosarcina</i>
Methylated Cl compounds	
4CH ₃ OH → 3CH ₄ + CO ₂ + 2H ₂ O	<i>Methanosarcina</i> and other methylotrophic methanogens
CH ₃ OH + H ₂ → CH ₄ + H ₂ O	<i>Methanomicrococcus blatticola</i> and <i>Methanosphaera</i>
2(CH ₃) ₂ -S + 2H ₂ O → 3CH ₄ + CO ₂ + 2H ₂ S	Some methylotrophic methanogens
4CH ₃ -NH ₂ + 2H ₂ O → 3CH ₄ + CO ₂ + 4NH ₃	Some methylotrophic methanogens
2(CH ₃) ₂ -NH + 2H ₂ O → 3CH ₄ + CO ₂ + 2NH ₃	Some methylotrophic methanogens
2(CH ₃) ₂ -N + 6H ₂ O → 9CH ₄ + 3CO ₂ + 4NH ₃	Some methylotrophic methanogens
2(CH ₃) ₂ NH ₃ Cl + 2H ₂ O → 3CH ₄ + CO ₂ + 4NH ₄ Cl	Some methylotrophic methanogens
Acetate	
CH ₃ COOH → CH ₄ + CO ₂	<i>Methanosarcina</i> and <i>Methanosaeta</i>

be reduced. Then the atomic content of different types was calculated as follows:

$$\text{Atomic content of types}(\%) (\text{ACT}) = (\text{Atomic content of nitrogen or sulfur from XPS}) \times (\text{Relative content of nitrogen or sulfur types}) \quad (1)$$

$$\text{Atomic content change of types}(\%) (\text{ACCT}) = (\text{ACT in residues}) - (\text{ACT in raw coals}) \quad (2)$$

After 36 days of fermentation, the ACT of N-5 in BY coal residues increased obviously, but decreased in QQ and ML coal residues. Compared to raw coal, the ACT of N-6 increases in BY coal residue and decreases in QQ and ML coal residues, and the ACT of the sum of N-5 and N-6 has an increase trend in BY coal residue and a decrease trend in QQ coal residue and ML coal residue (Fig. 11a). Thus, the BY coal residue should have changed to form fuel-NO_x more easily. Figure 11b shows that after 36 days of fermentation, the ACT of aliphatic sulfur in BY and ML coal residues has

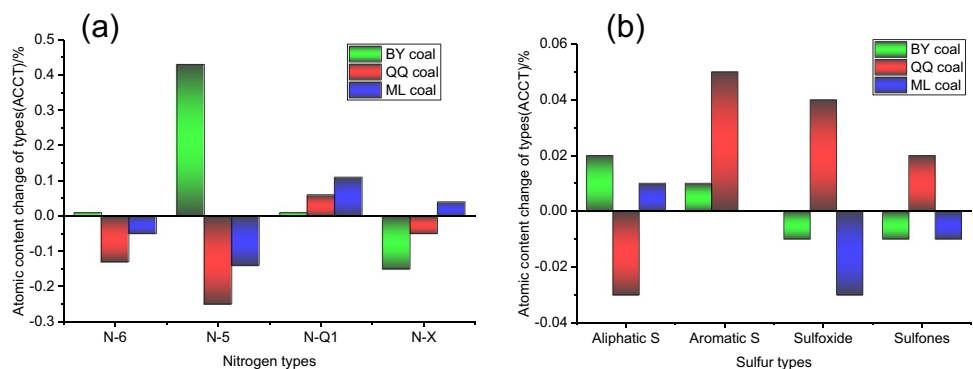
a rising trend, which indicates that the formation of SO₂ may be enhanced in the combustion of BY and ML coal residues;

the ACT of aliphatic sulfur in QQ coal residue has an obvious decreasing trend, which indicates that the formation of SO₂ may be weakened in the combustion of QQ coal residue.

Conclusions

The nitrogen and sulfur types in three coals before and after anaerobic fermentation were tested using XPS technology. The results show that the N-5 and aromatic sulfur are the

Fig. 11 The atomic content change of nitrogen types (a) and sulfur types (b) in coals



main nitrogen type and sulfur type respectively in coals. After anaerobic fermentation, the nitrogen and sulfur types have changed in the coal residues, and the low stability functional groups (such as N-5, aliphatic sulfur) in relatively low metamorphic coal (such as BY and QQ coal) have a larger content change than ML coal corresponding to the high degradation degree of relative low rank coals. The BY coal residue should tend to form fuel-NO_x more easily due to the increase of the N-6 and N-5. The fuel-NO_x may be reduced in QQ and ML coal residues due to decrease of the sum of N-6 and N-5. The formation of SO₂ may be enhanced in the combustion of BY and ML coal residues due to the increase of aliphatic sulfur. The results hint that when the biomethane yields in the coal seams or the biological gasification becomes an important part of the comprehensive utilization of coal, it would be necessary to evaluate the change of the nitrogen and sulfur types in coal residues.

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Author contribution HG designed research and performed research. XL analyzed data and wrote the paper. FZ reviewed the original draft. DX contributed to the revisions. ZD prepared the materials and reagents. ZL contributed to the art work. All authors read and approved the final manuscript.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Competing interests The authors declare no competing interests.

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